How To Evaluate and Improve The Stability of Fatty Foods

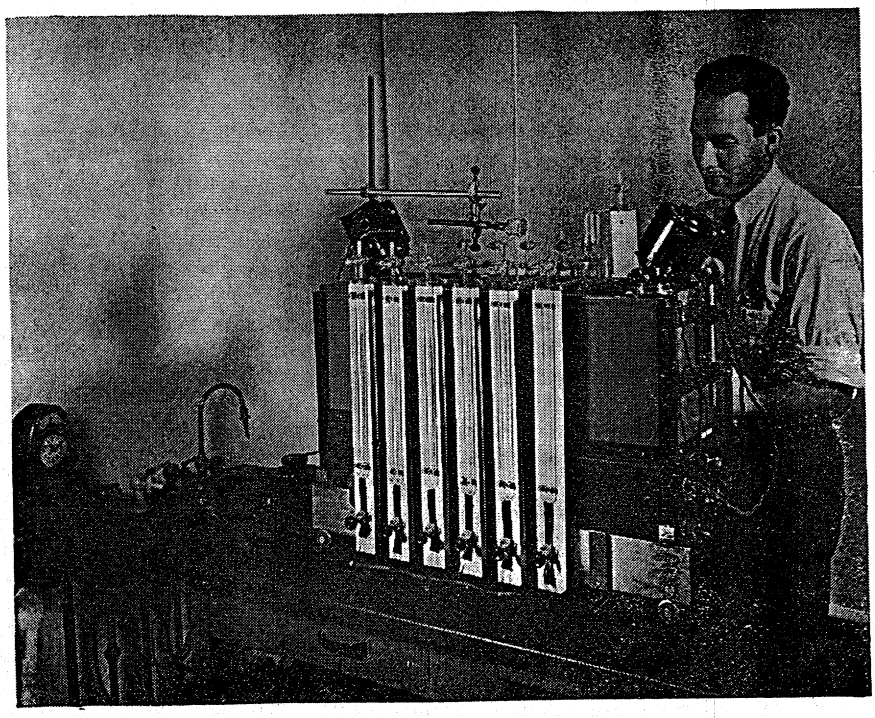
By R. W. RIEMENSCHNEIDER and WALDO C. AULT,
Eastern Regional Research Laboratory,* Philadelphia, Pa.

In this comprehensive discussion, the authors tell how to detect oxidative rancidity and make stability tests. They also describe antioxidants and outline their use for increasing the stability of fats and fatty foods

PREVENTION of rancidity is of great economic importance, not only in foods consisting principally of fat, such as lard and salad oils, but also in a large number of foods containing smaller proportions of fat. Among the latter are biscuit and pastry mixes, crackers, potato chips, dried milk and dried eggs, cereals and flours. Recognition of the vital importance of fats, oils and fatty foods in world economy has aroused interest in means for delaying or preventing rancidity in these materials.

Many different types of fat spoilage have been described in the literature.[1] The most important, however, are attributed to oxidation of the fat by atmospheric oxygen and may be referred to as oxidative rancidity. Air dissolved in the fat or in contact with its surfaces reacts with it, forming unstable oxygenated compounds. These compounds, which are peroxidic, undergo further oxidation and decomposition into the substances that are chiefly responsible for rancid odor and flavor.

Methods for detecting rancidity and for determining the stability or resistance of the product to oxidation, and a discussion of means for delaying or preventing these undesirable changes, form the basis of this paper. The term *rancidity* as used here refers only to *oxidative rancidity*, unless otherwise qualified. Emphasis is placed primarily on fats and oils rather than on innumerable products containing fat, because to a large extent, the stability of these products to oxidative rancidity depends upon the stability of the fat contained in them.



Barcroft-Warburg apparatus used in the oxygen absorption method for measuring fat stability.

Detection of Rancidity

The complex chemical changes involved in the oxidative deterioration of fats are not completely understood. Moreover, the nature of these oxidative changes may vary considerably from one substrate to another, particularly under variable conditions of exposure to heat, air and light, thus giving rise not only to different proportions of the decomposition products but, in some cases, to entirely different products. Despite the complexity of the oxidative reaction and the multiplicity of reaction products, the typical odor and flavor of rancidity seem to be definitely associated with the presence of aldehydic substances, and some of the chemical methods for the detection of rancidity are in reality aimed at qualitative or quantitative estimation of this class of compounds.

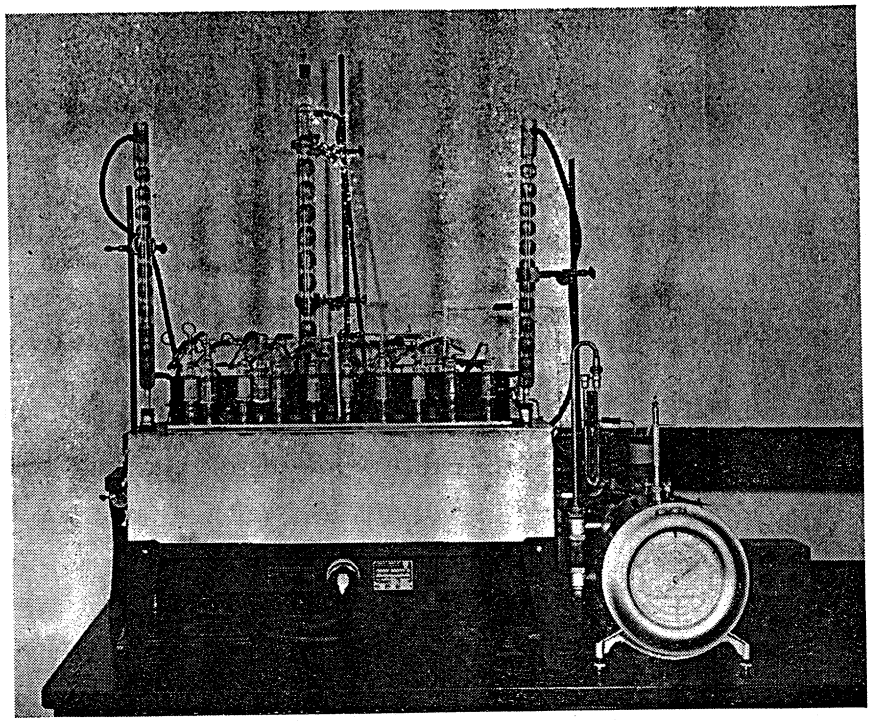
Ability of individuals to detect the typically unpleasant odor or taste characteristic of rancid substances may vary considerably; even the same person may vary in this respect from time to time. Moreover, these qualities do not lend themselves readily to either qualitative or quantitative description. For these reasons, much effort has been devoted to the development of chemical tests for detecting rancidity, and although none of the tests proposed to date correlate as well as is desirable with actual organo-

*One of the laboratories of the Bureau of Agriculture and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

leptic tests, the use of one or more of them for confirmatory purposes is recommended.

Organoleptic tests for odor and flavor are considered to be the most important and reliable means of detecting rancidity, even though numerous chemical tests have been proposed. Suggestions helpful in the selection of individuals who are above average in sensitivity to odors and flavors have been reported.[2,3] For practical reasons, it may be necessary to limit the number of individuals on the tasting panel to three, and preferably to those who have acquired considerable experience and interest in rancidity problems. Certain factors, such as temperature of the sample, limitation on time to avoid sensory fatigue, and environmental conditions, should be standardized insofar as possible.

Chemical methods for detecting rancidity have been reviewed extensively by Lea.[1] Only a few of the more widely used methods will be discussed here. The Kreis test consists of treating the sample of fat with concentrated hydrochloric acid and a solution of phloroglucinol. A positive reaction depends upon the presence in the fat of epihydrin aldehyde, its acetal or precursors of this aldehyde. The red color formed in the reaction is attributed to a condensation product of epihydrin aldehyde with phloroglucinol. Quantitative measurements of this color may be made by comparing it with Lovibond glass color standards[4] or by the use of a photometer.[5] It has been shown that during the induction period (prerancid period) the development of color, shown by the Kreis test, parallels the development of fat peroxides. This suggests the possibility that the hydrochloric acid used in the test may react with the fat peroxides to form compounds of similar character to epihydrin aldehyde. Certain crude vegetable oils, even when fresh, contain interfering substances which give a red color with phloroglucinol. This limitation is not serious, however, since refined oils and animal fats are more likely to require examination, and these do not contain the reacting substances. In our experience, every rancid fat has given a positive Kreis reaction. For most satisfactory application of the test, it should be calibrated against odor and flavor under the particular set of conditions of aging and on each type of fat. In this way, a definite color intensity may be established to serve as an indication of rancidity.



Swift stability apparatus used in the active oxygen method for measuring fat stability.

The peroxide value[6] also has been used extensively as a guide in the detection of rancidity. Like the Kreis color, the peroxide value should be calibrated against odor and flavor for the particular type of fat and set of conditions. Thus a peroxide value of 20 milliequivalents ordinarily is a satisfactory "end point" for lard, provided the sample has been under observation during the fresh stage. The peroxide value, however, should not be relied upon for the detection of rancidity in miscellaneous samples of unknown history and treatment; for example, the distinctive flavor and odor caused by exposure of fats to light, even diffuse daylight, does not seem to be correlated with the peroxide value.

The Schiff reaction for aldehydes[7] and modified Schiff test[8] may also be used to supplement other chemical and organoleptic evaluation of fats. They are also subject to the same limitations as the peroxide value and the Kreis test. None of these chemical tests should be made the only criterion of rancidity, but they are helpful in confirming the organoleptic judgments.

In certain products—for example, cereals, flours and crackers—it may be necessary to extract the fat from the sample with a solvent before carrying out chemical tests for rancidity. Anhydrous peroxide-free ethyl ether is reasonably satisfactory for this purpose, provided proper precautions are taken to avoid undue exposure of the fat to heat and air. Cold extraction and removal of the solvent under reduced pressure is desirable.

Stability Tests

More important to industry than merely the detection of rancidity are means of determining the stability of fats and fatty products. To avoid confusion of terminology, in this paper stability is defined as resistance to oxidative rancidity and may be expressed as the time required under specified conditions for the fat or fatty product to become rancid in odor or flavor. It is often impracticable, however, to determine the stability under actual conditions of commercial storage and merchandising because of the long time required in many instances for rancidity to develop. Moreover, these actual conditions — temperature, moisture, exposure to light and type of package—usually are variable. For these reasons a great deal of effort has been expended in attempts to devise rapid methods for determining stability. In these methods, the conditions of accelerated aging should be reproducible and permit relative stability evaluations, often within a working day.

Probably the simplest of the commonly used rapid stability determinations consist of heating the sample in a hot-air oven and examining it at intervals for rancid odor and flavor. With careful attention to standardization of conditions, fair reproducibility of results can be obtained. In different laboratories, however, results often are not com-

parable because of lack of uniformity of the ovens, containers and sample sizes employed for this purpose and also because of rather large personal errors involved. The personal error may be diminished by using a chemical method, such as the peroxide value, to indicate the end point of the induction. The specific conditions for this method known as the Schaal oven test are perhaps the most commonly employed, although for the more stable shortenings the test often requires a month or more.[9] This time can be greatly shortened by using smaller samples or larger vessels, thereby increasing surface exposure to air, and also by raising the temperature, though the results obtained under the more drastic conditions probably will show less correlation with actual storage data. Oven incubation is particularly adaptable for determining the stability of fat-containing products such as pastry, crackers, cookies, cereals and flours.

Another rapid method, commonly referred to as the Swift stability test,[10] has been used extensively, at least in this country. A uniform flow of washed air is bubbled through the sample, which is maintained at constant temperature by means of a boiling-water bath. The progress of oxidation is followed by periodic organoleptic tests and determinations of peroxide content. Under the conditions employed, rancidity in lard can usually be detected at a peroxide level of 20 milliequivalents per kilogram; this end point may be considerably different for other types of fats and oils. It is convenient to express the stability as the time required for the fat to attain the predetermined peroxide level. Several recent improvements in the apparatus and modifications of the procedure have been proposed.[11,12] This method has advantages over oven incubation. The sample can be maintained at a uniform and reproducible temperature; and the air and liquid fat are in equilibrium owing to saturation of the fat by continuous stirring with air, thus making reproducibility less dependent upon exactness of the ratio of surface exposed to the weight of the sample.

Measurement of oxygen absorption of fats as a means of determining their comparative stabilities is preferred by some investigators. For this purpose, the apparatus need not be complex. Simple types such as have been described[13,14,15] seem to be adequate. For comparison of results between different laboratories, however, it would be advantageous to have an accepted standard apparatus and procedure. The particular oxygen-absorption apparatus and procedure used should be calibrated for each type of fat or product in order to establish a satisfactory end point for the induction period. The time required for the sample to absorb a preestablished amount of oxygen per unit weight of sample is taken as the stability. One disadvantage of the oxygen-absorption method is that organoleptic tests cannot readily be made at intervals during the period of oxygen absorption without interfering with the manometric measurements. Oxygen-absorption technics have been used to determine the stability of certain dry fat-containing products, such as dried milk[13] and crackers.[16]

A number of other rapid methods for determining stability have been proposed but have not been used extensively, either because they are too complicated to be practicable or because they have not been thoroughly investigated. One fault in common with even the generally accepted methods is that they give only relative values under the empirical conditions of the test and may not bear a constant relationship to values obtained under other conditions, such as storage. Despite these inadequacies, however, methods for determining stability are valuable to industry as a guide in improving plant processes, in evaluating antioxidants and in maintaining standards of quality.

Increasing Stability

There are several practical approaches to the problem of delaying or preventing oxidative rancidity. Proper choice of raw materials and careful attention to processing conditions, with a view to eliminating or reducing exposure to air, light, excessive temperatures and contamination, particularly by metals, should be stressed as of first order in importance. Partial hydrogenation of products which are essentially pure fats almost invariably increase their stability. Packaging the finished product in such a manner as to exclude air and light will, of course, afford a considerable measure of protection.

Often, however, greater stability than can be obtained within the practical limitations of these methods will be desirable or necessary. In such cases antioxidants may be used. *In fact, in many cases the use of antioxidants appears to offer the greatest hope of a solution of the economic problem of oxidative rancidity.* In addition to being reasonably effective in delaying rancidification, an antioxidant for foods should possess a number of properties, which may be outlined briefly as follows:

It must have neither acute nor chronic toxicity in quantities considerably greater than those likely to be used, even when ingested over long periods of time.

It should have at least sufficient solubility in fat to facilitate its use; appreciable solubility will usually be advantageous.

It should not impart any objectionable odor, color or taste to the product either when freshly prepared or after storage.

It should be stable to whatever processing conditions the food in which it is used will be subsequently subjected.

It should be relatively inexpensive and available, or at least potentially available, in relatively large quantities.

Despite this imposing list of requirements, considerable progress has been made in this field. The granting of permission by the Meat Inspection Division of the War Food Administration to use four different antioxidant substances in lard, provided suitable declaration is made on the label, may be taken as an indication of this progress. These antioxidants are gum guaiac, lecithin, a concentrate of tocopherols in vegetable oils, and nordihydroguaiaretic acid (N.D.G.A.) The importance of these materials warrants a brief description of each.

Gum Guaiac—Gum guaiac, the resin from an evergreen tree indigenous to the West Indies, is chiefly produced in eastern Haiti. It is relatively inexpensive. The use of gum guaiac as an antioxidant in fats and oils was first disclosed in a patent[17] assigned to Swift & Co. It contains complex phenolic constituents, for example, guaiaretic acid, and presumably its action as an antioxidant is due to one or more of these substances. As might be expected from its chemical nature, it is an effective antioxidant and has been used commercially. The protective effect of gum guaiac is reported to carry over into baked goods such as piecrust and crackers.

Lecithin—With the development of the soybean processing industry in this country, large quantities of "commercial lecithin" became available at reasonable prices. Because of its wide occurrence in many

foods, there is no question about the edibility of lecithin. Because of its protective and emulsifying properties, it has been added to foods for a considerable period of time. When evaluated by any of the accelerated stability tests discussed previously, lecithin usually is less effective than many of the other antioxidants, particularly those of the phenolic type. Too little information is available to say whether lecithin is less effective under actual storage conditions. When used in conjunction with tocopherol or polyphenolic antioxidants, lecithin frequently enhances the stability beyond expected values. A disadvantage of lecithin in shortening fats is its tendency under certain conditions to cause darkening and foaming, particularly when used for deep-fat frying.

Concentrate of Tocopherols in Vegetable Oils—A preparation consisting of 30 percent concentration of tocopherols in vegetable oil may be added as a preservative to lard and rendered pork fat in quantities up to 0.1 percent. Tocopherols, of which there are three, the alpha, beta and gamma, are probably the most important naturally occurring antioxidants in vegetable oils. They have nutritional significance, particularly the alpha variety, which is vitamin E. They are readily soluble in fats and oils and are effective antioxidant substances, particularly when used with a partly hydrogenated substrate or in conjunction with an acidic-type antioxidant. Most vegetable oils contain significant amounts of tocopherols, and as a result have greater stability than animal fats of similar iodine value. Further addition of tocopherol to vegetable products usually results in only small increases in stability.

Insofar as we are aware, such a concentrate is prepared commercially at present only by the application of a molecular distillation process to tocopherol-bearing oils. Work recently reported from the Southern Regional Research Laboratory[18] indicates that such concentrates can be prepared by low temperature crystallization technics.

Nordihydroguaiaretic Acid (N. D. G. A.)—This phenolic substance and its antioxidant action has been discussed by Lundberg, Halvorson and Burr.[19] These investigators have stated that it is readily obtained in substantial yield from *Larrea divaricata* (one of several plants known as creosote bush) and that it compares favorably with other highly effective inhibitors of the phenolic type. They further report that the protective effect is to some extent carried over into baked products.

Other Antioxidants — Many antioxidants, in addition to those approved by the Meat Inspection Division, have been disclosed in the literature. A few that have attracted considerable attention will be discussed briefly. In general, the polyphenolic compounds that have hydroxyl groups in ortho or para relation to each other are most effective; as examples may be mentioned hydroquinone, 1,2,4-hydroxyhydroquinone, gallic acid and its esters, pyrogallol, catechol and dihydroxynaphthalenes. It is hardly possible to give an accurate comparison of the relative effectiveness of these antioxidants because there is no suitable basis at present for a quantitative interpretation of results reported by different investigators. It should be emphasized, moreover. that much more practical work is required before any conclusions can be drawn as to the suitability of these compounds as antioxidants for edible products.

Mention has previously been made of a 30 percent concentrate of tocopherols in vegetable oil. It has been shown also that a substantial increase in stability of animal fats, such as lard, can be achieved without necessitating any costly isolation or concentration of the tocopherols, merely by the addition of about 5 to 10 percent of tocopherol-bearing oils or their hydrogenated products. Synthesized compounds similar to tocopherol, hydroxychromans and related compounds have been found to be effective antioxidants.[20]

Another class of compounds, at times referred to as acidic antioxidants, has aroused considerable interest in recent years. Among the better known of these may be mentioned phosphoric acid and some of its esters, ascorbic acid, fatty acid monoesters of ascorbic and iso-ascorbic acids, citric and tartaric acids, and many other hydroxy carboxylic acids. When added to substances containing tocopherol or an antioxidant of the polyphenolic type, these acidic substances seem to enhance or reinforce the antioxygenic action, with the result that greater increases in stability, as determined by the usual rapid tests, are obtained than would be expected from a summation of the effects of each used alone. As would be expected, such synergists usually are especially effective when added to the tocopherol-bearing vegetable oils or their hydrogenated products. There seems to be some question as to whether these acidic substances should be considered as antioxidants, because they show little or no protective effect when added to fat or fat esters that have been treated to remove natural antioxidants normally present. Hence, the term *synergist* may be more properly applied. It has not been determined whether this synergistic effect, noted in rapid tests, has real significance under actual storage conditions or whether this apparent protective effect carries over into baked goods. Many of these compounds undergo decomposition at high temperatures, particularly at deep-fat frying temperatures, and cause darkening of the fat.

The use of special flour, or of an extract of cereal flours, may have advantages, particularly in certain foods. It has been suggested for example, that the flour may be incorporated with fat to be used as shortening for baked goods or added directly to such products as margarine, ice cream and salad dressings. It is claimed also that parchment paper into which such flour has been incorporated retards the development of rancidity when used for wrapping fatty foods.

It should be emphasized that even the best antioxidant should not be regarded as a cure-all. It will not make a poor product into a good one nor will it cover up the effects of mishandling and careless processing. The amount or proportion of antioxidant to use in a given product is important. If too much is used, off-flavors and odors may frequently be detected long before the characteristic rancidity develops. The amount of antioxidant used should be the minimum needed for a reasonable storage or shelf life of the product. Progress in the practical solution of the problem of rancidity in any product will undoubtedly result from continued research on processing technology, on application of antioxidants and on packaging.

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